Production of brown algae pyrolysis oils for liquid biofuels depending on the chemical pretreatment methods

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ABSTRACT

Based on observations of rapidly growing biochar in fluidization beds, kelp (*Saccharina japonica*), a species of brown algae, was pretreated for the efficient operation of pyrolysis processes to produce pyrolysis oils. The removal of catalytically active inorganic minerals and the softening of polymeric seaweed structures were performed by means of chemical treatments, including a $CaCl_2$ treatment to isolate valuable and sticky fucoidan and a sulfuric acid treatment to remove catalytically active minerals. The sulfuric acid pretreatment significantly reduced the inorganic elements but did not significantly affect the properties of the pyrolysis oil compared to the non-treated kelp pyrolysis oil. Whereas the non-treated kelp produced significantly large chunks of biochar, which hindered the continuous operation of pyrolysis, the kelp treated with sulfuric acid did not produce aggregated large particles of biochar, thereby offering a means of developing reliable continuous pyrolysis processes.

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1. Introduction

Macroalgae are promising biomass resources because of their rapid growth, less competition with foods, and cultivation in the sea. Brown algae, *Saccharina japonica (S. japonica),* used in this study is composed of alginate, laminarin, fucoidan, mannitol, and other inorganic elements [1]. Because other biomass sources, such as corn, sugarcane, wood, and grass, have been fermented into bioethanol and other bioalcohols, there have also been efforts to ferment macroalgae into bioalcohols [2,3]. Although bioalcohol production, one of the frequently used biofuel processes, can be selected for the macroalgae feedstocks, the smaller amount of fermentable sugars compared to cellulosic or carbohydrate types of biomass may hinder the use of macroalgae as a feedstock for bioalcohol production [1].

Under these circumstances, thermochemical conversions, including pyrolysis and hydrothermal liquefaction, have been sug-gested to obtain hydrocarbon fuels from macroalgae [4], and thermochemical conversions of microalgae have been widely investigated in studies pertaining to microalgae-based biodiesel production [5–7]. As lignocellulosic biomass is processed [8], batch or fixed bed pyrolysis [9–12], continuous flow pyrolysis using a fluidized bed reactor or others [13–18], and batch hydrothermal liquefaction [19,20] have been assessed for the ability of these methods to produce bio-oils. The addition of a special treatment, such as a microwave treatment, was performed to valorize macroalgae-derived pyrolysis oils [4,12,21,22]. The kinetics of the combustion and pyrolysis of seaweeds was also studied in an effort to understand the thermal degradation characteristics [23–28].

In keeping with the research on producing pyrolysis oils using organic components in seaweeds, the production of the pyrolysis oils of *S. japonica* using a fluidized bed reactor was attempted, but rapidly growing biochar chunks were observed in the early stage of the process (see Fig. S1 in the supplementary information), which made it difficult to operate the process continuously. It was predicted that the robust char formed possibly because of the inorganic mineral-catalyzed gelation and then the carbonization of gel-like sticky organic polysaccharides, which was similar to observations of lignin pyrolysis [29]. To increase the pyrolysis oil

yield, the removal of the major organic components of macroalgae, including alginate, laminarin, and mannitol was avoided. Two pre-treatment methods were selected: a sulfuric acid and a $CaCl_2$ treatment. The sulfuric acid pretreatment of macroalgae was performed to remove a significant amount of the inorganic elements by exchanging metal cations with protons to convert the inorganic salts of alginates and fucoidan to acidic forms and thus to reduce the catalysis caused by these materials during the pyrolysis process. Because the inorganic elements do not contribute to the yields of macroalgae pyrolysis oils, the removal of these inorganic elements may improve the pyrolysis processability. A $CaCl_2$ treatment of macroalgae has been used to extract valuable fucoidan [30] and soften the networked structures of macroalgae [31]. The relatively small component (5–20 wt%) fucoidan was removed to suppress the gelation of organic components. In addition, because fucoidan is a valuable chemical that is extracted from seaweeds, this process can simulate the valorization of fucoidan-extracted seaweeds by pyrolysis. The removal of significant amounts of metal elements was also predicted because fucoidan exists as metal salts [1].

2. Experimental section

2.1. Materials

Kelp (*S. japonica*) was collected at Wando, Korea. Kelp was sieved to 600–1000 μm and dried at 60 °C for 24 h prior to use. Calcium chloride ($CaCl_2$, anhydrous, 95.0%) was purchased from Wako (Osaka, Japan). Sulfuric acid (98.8%), D-mannitol, sodium alginate, laminarin (*Laminaria digitata*), fucoidan (*Fucus vesiculosus*), and tetrahydrofuran were purchased from Aldrich (Milwaukee, WI, USA). Deionized water (DI water, 18.2 MΩ cm) was prepared using an aquaMAX Ultra 370 water purification system (YL Instruments, Seoul, Korea).

2.2. Pretreatment of the kelp

Kelp was processed with (i) a $CaCl_2$ treatment (fucoidan removal) and (ii) a sulfuric acid pretreatment. (i) Fucoidan removal was performed by stirring the sieved kelp powder (420 g, 600–1000 μm) mixed with an aqueous calcium chloride solution (1 wt% $CaCl_2$, 7 L) twice for 20 min each. The mixture was then filtered, washed with DI water, dried at 105 °C for 24 h, and stored in a desiccator (KelpF) [30]. (ii) The acid pretreatment was performed by stirring the sieved kelp powder (700 g, 600–1000 μm) mixed with an aqueous sulfuric acid (4 wt% H_2SO_4, 7 L) solution for 30 min. This mixture was then filtered and washed with DI water to achieve a pH of 5.5. The washed product was further dried in air at 105 °C for 16 h and stored in a desiccator (KelpA).

2.3. Pyrolysis

Pyrolysis of the kelp was performed using batch and continuous reactors (Fig. 1). When the fixed-bed-type batch reactor (quarts, ID = 2.4 cm) was used (Fig. 1(a)), each run processed 40 g of kelp powder pre-dried in air at 105 °C. The reaction was processed under an N_2 flow (0.5 L/min) at 470 °C for 10 min. The pyrolysis oil was collected at the first (25 °C) and second condensers (0 °C). The continuous flow pyrolysis reaction was performed using a fluidized bed reactor (Fig. 1(b)). Pre-sieved kelp powder (600–1000 μm) was dried in air at 105 °C and conveyed using a screw-type solid feeder at a rate of 150 g/h to a reactor filled with alumina particles (260 μm). The N_2 carrier gas flow rate was fixed at 45.37 L/min (at 470 °C). The residence time of the kelp particles in the reactor was held to 2 s or shorter. The formed char particles were collected at the cyclone, and the volatile products were collected using two chilled condensers (first condenser at 22 °C; second condenser at −10 °C).

2.4. Characterization of kelp powders and pyrolysis oils

For all the GC/MS analyses, the concentrations of the identified materials were determined using the relative peak areas [28,32]. The prepared kelp powder was observed by means of Py–GC/MS, which was performed using an Agilent 6890 GC equipped with a CDS pyroprobe 5000 and a 5973 mass selective detector. The pyroprobe was operated at a ramping rate of 450 °C/s to reach a temperature of 450 °C and hold it there for 20 s; it was thermally protected by the surrounding air at 270 °C. GC/MS was performed using a DB-1701 capillary column (60 m × 0.25 mm × 0.25 μm) [33]. The pyrolysis oil was observed using a GC/MS (the Agilent Technologies 7890A GC system with a HP-5MS column, 60 m × 0.25 mm × 0.25 μm). Prior to the GC/MS analysis, the pyrolysis oil was mixed with tetrahydrofuran to form a 50% w/w mixture, after which a biphasic mixture composed of a transparent bottom and dark top layer formed, whose GC/MS results were separately obtained. The amount of volatile compounds in the kelp powder was measured by means of a proximate analysis under an air flow using a TGA SDT Q600 instrument (TA Instruments). The kelp powder (∼15 mg) was heated to 120 °C at a ramping rate of 10 °C/min and kept at 120 °C for 30 min, heated to 575 °C at 10 °C/min and kept at 575 °C for 30 min, and then heated to 800 °C at 10 °C/min and kept at 800 °C for 30 min. The weight losses up to 120 and 575 °C were attributed to water and volatile compounds, respectively. The remaining weight was assigned as ash. Thermogravimetry of the kelp powders, oils, and other compounds was performed under an N_2 flow using a TGA SDT Q600 instrument (TA Instruments). The compositions of C, H, N, and S in the kelp powders and oils were measured using a Flash 2000 series CHNSO analyzer (Thermo Scientific, USA). The oxygen content was measured using a Fisons-EA-1108 (Thermo Scientific, USA). The inorganic compositions of the kelp powders and oils were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Polyscan-61E, Thermo Electron Corp., Winsford, Cheshire, UK). To measure the solid contents in the pyrolysis oils, the oil (5 g) was dissolved in a mixture of dichloromethane and methanol (50% w/w, 50 g), which was stirred for 30 min. The resulting mixture was filtered using a paper filter (0.45 μm) and dried in air at 60 °C for 24 h prior to the measurement of the remaining weight. The total acid number (TAN) of the oil was measured by stirring the oil (0.05 g) dissolved in acetone (20 mL) for 10 min. Three drops of phenolphthalein (0.1 g) dissolved in methanol (20 mL) were added to the oil/acetone solution, which was titrated with 0.1 M KOH, and the TAN was determined as TAN (mmol KOH/g) = (KOH volume, mL) × (0.1 mmol/mL KOH)/(weight of oil, g). The thermogravimetry results for the kelp and pyrolysis oil were obtained using the TGA SDT Q600 instrument; this process was performed in an N_2 flow by heating ∼15 mg of the sample to 1000 °C at a ramping rate of 20 °C/min. FT-IR was performed on the kelp powder using a Nicolet iS10 FT-IR system. The Karl Fischer titration method was used to measure the water content of the pyrolysis oil (3 mg) using a Karl Fischer Moisture Titrator MKC-520 with the addition of HYDRANAL-Coulomat AG-H. For the bi- or multi-phasic oil mixture, each phase was separately observed. The viscosity of the pyrolysis oil was measured at 25 °C using an AR2000 (TA Instruments, New Castle, DE, USA) cone and plate stress control type rotational rheometer. The shear rate was 0.1–1000 s^{-1}. The density of the pyrolysis oil, prepared by stirring for 30 min, was measured using a pycnometer (Lenz Laborglas, Wertheim, Germany). The heating values of the pyrolysis oils were determined using the DuLong equation [34]: HHV (higher heating value, MJ/kg) = 33.742 × [C] + 143.905 × ([H] − [O]/8) + 9.396 × [S], where [C], [H], [O], and [S]
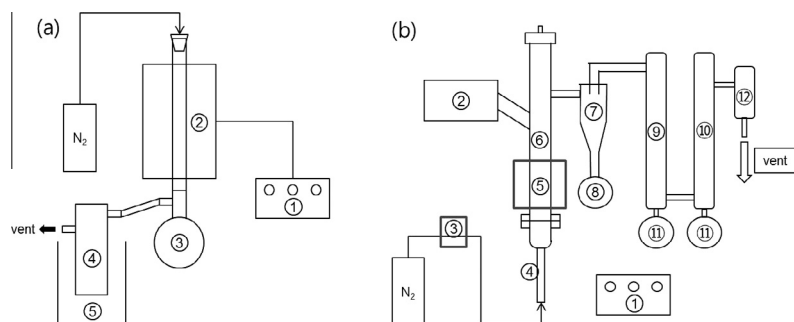
Fig. 1. Schemes of (a) batch (1: controller, 2: reactor, 3: first condenser, 4: second condenser, 5: ice bath) and (b) continuous pyrolysis reactors (1: controller, 2: screw feeder, 3: MFC, 4: air heater, 5: ceramic heater, 6: reactor, 7: cyclone, 8: char collector, 9: first condenser, 10: second condenser, 11: oil collector, 12: filter).

are the mass fractions as measured through elemental analysis [19,20,35–39].

3. Results and discussion

3.1. Screening pretreatment methods

To find the optimum pretreatment methods, thermogravimetry (TG) was performed on the kelp powders (Figs. 2 and S2). The pretreatment methods that exhibited less ash and more weight loss up to 500 °C were selected to produce less char and more pyrolysis oil. Kelp powders treated with an aqueous sodium hydroxide (4 wt% NaOH) solution, an aqueous ammonia (4 wt% NH$_3$) solution, an aqueous sulfuric acid (4 wt% H$_2$SO$_4$) solution, and DI water were observed with TG, and the lowest amount of ash formed after the sulfuric acid treatment (Fig. 2(a)). In comparison with the sulfuric acid treatment method, kelp powder treated with the aqueous NaOH and NH$_3$ solutions became a sticky gel-like material that could not be used in the pyrolysis reactor. After observing the effects of an acid treatment on the increase in the volatile compounds, a pretreatment using an aqueous hydrochloric acid (HCl) solution was also attempted, but there was not a significant difference between the H$_2$SO$_4$ and the HCl treatment methods (Fig. 2(b)). The concentration of H$_2$SO$_4$ was also decreased from 4 to 1 and 0.4 wt%, but the amount of remaining ash increased with the more diluted H$_2$SO$_4$ solution (Fig. 2(c)). An extension of the treatment time from 1 to 24 h and an increase in the reaction temperature from 25 to 75 °C were attempted, but they did not exhibit significantly different TG behavior (Figs. 2(d) and (e)). Washing the kelp powder pretreated with sulfuric acid was attempted using DI water and ethanol, and the kelp powder washed in this manner produced the least ash (Fig. 2(f)). These screening attempts determined the optimum pretreatment conditions, as described in Section 2.2. The pretreatment of kelp powder using strong acids may damage the structure of carbohydrates, as reported for cellulose, although the distortion of the kelp structure by acids was not clearly observed because kelp powder was amorphous and its morphology did not exhibit a significant difference [40]. In addition to the sulfuric acid pretreatment method, the CaCl$_2$ treatment method was utilized, which has been reported as useful for extracting the valuable fucoidan from the macroalgae [41]. Via the CaCl$_2$-treatment, the softening of the macroalgae structure was expected because of the extraction of fucoidan.

3.2. Characterization of pretreated kelp

The non-treated (Kelp) and pretreated kelp powders (KelpF and KelpA) were characterized by proximate and elemental analyses to determine the properties of these feedstocks. The proximate

analysis indicated that the acid pretreatment significantly reduced the amount of ash, mostly minerals, while also increasing the amount of volatile organic compounds (KelpA, Table 1). Because of the possible removal of inorganic elements, the amount of carbon composition of KelpA also increased. The aqueous CaCl$_2$ treatment to remove fucoidan also increased the amount of carbon composition because the sulfuric acid functionality of fucoidan exists as a salt of metals (KelpF, Table 1) [1]. The removal of inorganic elements was also confirmed with elemental analysis, which exhibited the decreasing concentrations of Na, Mg, and K for both KelpF and KelpA (Table 1). In spite of the pretreatment, the initial HHVs of the kelp feedstocks were as low as 12.1–14.4 MJ/kg, regardless of pretreatment.

Based on these properties, the thermal degradation of the non-treated and pretreated kelp powders was observed using thermogravimetry, exhibiting different behaviors depending on the pretreatment method (Fig. 3). KelpA produced greater amounts of volatile compounds up to 600 °C (Fig. 3(a)) because it contained less ash-producing inorganic elements, as listed in Table 1. Based on the thermogravimetry results of the commercially available single components (Fig. 3(b)), the degradation at 200–400 °C can be attributed to the degradation of alginate, laminarin, fucoidan, and mannitol. In comparison with the thermal degradation of commercially available fucoidan and laboratory-prepared kelp-extracted fucoidan, both of which exhibit degradation at 600–800 °C, it was confirmed that fucoidan was extracted by the CaCl$_2$-treatment (Figs. 3(a) and (c)). The extraction of fucoidan during the CaCl$_2$ pretreatment of the kelp powder was also confirmed by means of the FT-IR of the extracted products, exhibiting S=O (1225 cm^{-1}) and C—O—S (830 cm^{-1}) absorption peaks, which were observed for the commercially available fucoidan powders (Fig. S3).

Py—GC/MS of the treated and non-treated kelp was conducted to identify the volatile compounds that may be collected as pyrolysis oil components (Fig. S3 and Table S1). When heated to 450 °C, no significant difference in the product distribution was observed between Kelp, KelpF, and KelpA. Most products, including isosorbide, furan derivatives, hydroxyl propanone, and allose, were obtained from the carbohydrates in macroalgae. Long-chain hydrocarbons, including tetradecanoic acid, hexadecanoic acid, and octadecanoic acid, were observed, which had to be obtained from the lipids in the macroalgae.

3.3. Batch pyrolysis

The pyrolysis oils of Kelp, KelpF, and KelpA were obtained using the fixed-bed-type batch system depicted in Fig. 1(a). Two condensers collected the oils at the highest yield (37.9%) when the non-treated kelp was processed. Although slightly less, KelpF and KelpA produced 28.6% and 33.3% yields, respectively. When the pyrolysis oil was collected at two subsequent condensers, the
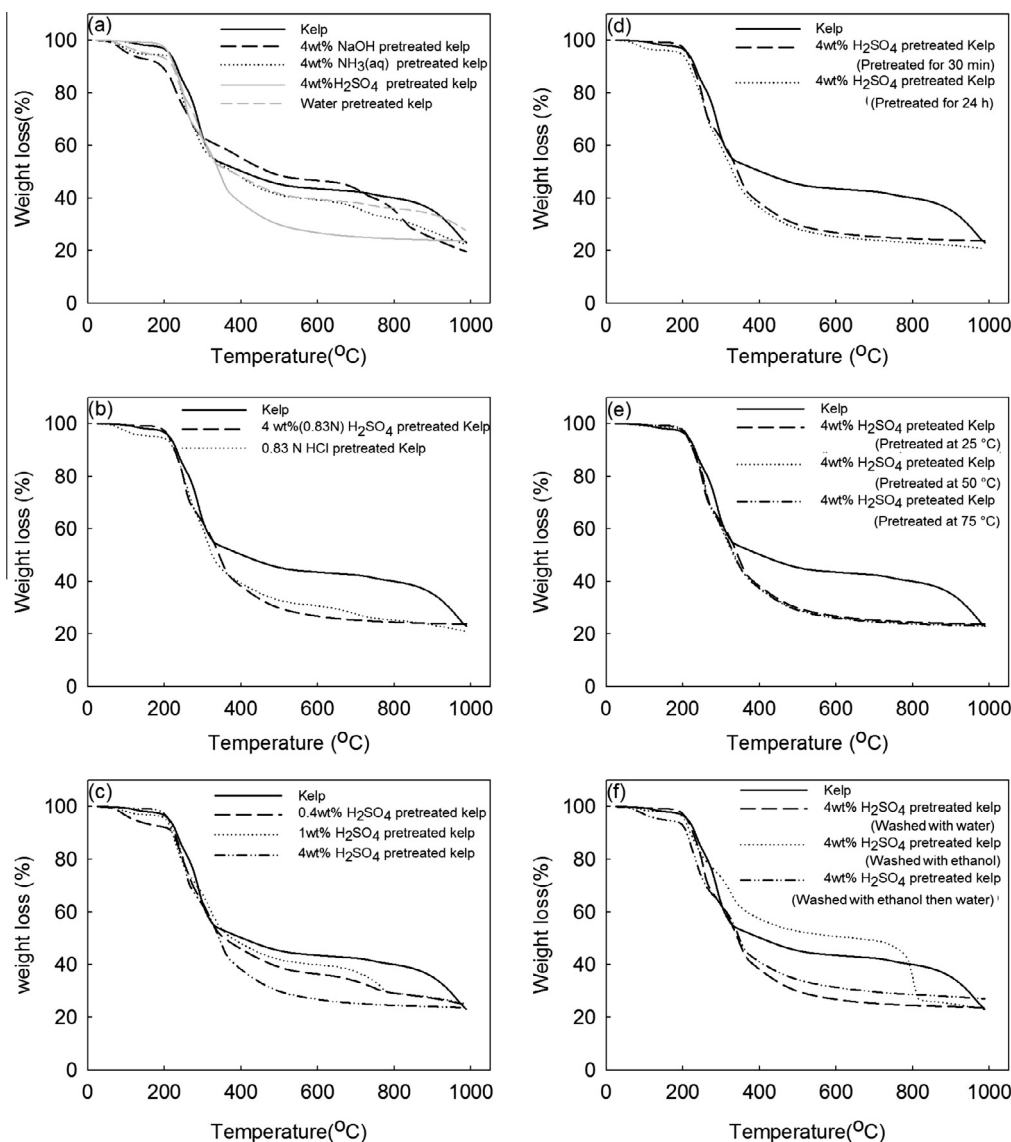
Fig. 2. Thermogravimetry results of kelp powder depending on the pretreatment conditions: (a) solvent, (b) acid, (c) acid concentration, (d) pretreatment time, (e) pretreatment temperature, and (f) washing solvent.

Table 1
Properties of kelp powders.[a]

	Kelp (*S. japonica*)	KelpF	KelpA
Proximate analysis (wt%)			
Moisture	7.4	1.6	6.7
Volatile	74.3	83.1	90.0
Ash	18.3	15.4	3.3
CHNSO analysis (wt%)			
C	34.7	39.4	44.3
H	5.5	5.3	5.6
N	1	1.5	1.6
S	<0.3	<0.3	<0.3
O	41.6	39.6	47.6
O/C (mol/mol)	0.90	0.75	0.81
H/C (mol/mol)	1.90	1.61	1.52
Apparent density (g/cm^3)	0.56	0.53	0.56
HHV (MJ/kg)	12.1	13.8	14.4
Inorganic elements (ppm)			
Na	High	871	1778
Mg	3584	695	522
K	High	1737	4587
Ca	High	High	High

[a] Calculated with dry basis.

densities of the condensed oils were not significantly different, with the result showing 1.02–1.13 g/cm^3 (Table 2). A high water content (34.7–82.4 wt%) was measured for all of the kelp oils. It must be noted that the oils obtained from the CaCl$_2$- and the acid-treated kelp powders (KelpF and KelpA) contained very high amounts of water (64.8–82.4 wt%). It was observed that the oil (collected at the first condenser from the kelp) with the lowest amount of water exhibited the highest density, whereas the others had densities very close to that of water. All of the oils collected at the condensers underwent phase separation to form dark and transparent phases with ambiguous interfaces (Fig. S4). This phenomenon has been reported for lignocellulose pyrolysis oils [42]. Whereas the kelp oil collected at the first condenser exhibited dark and transparent phases on the top and bottom layers, respectively, the other oils exhibited a dark phase on the bottom layer and a transparent phase on the top layer. The solid contents suspended in the oils were 0.030–0.290 wt% for all oils. When the total acidity was measured with KOH titration, the TANs of the oils were 33–129, which was slightly lower than the TANs reported for lignocellulose pyrolysis oils (84–166) [43].
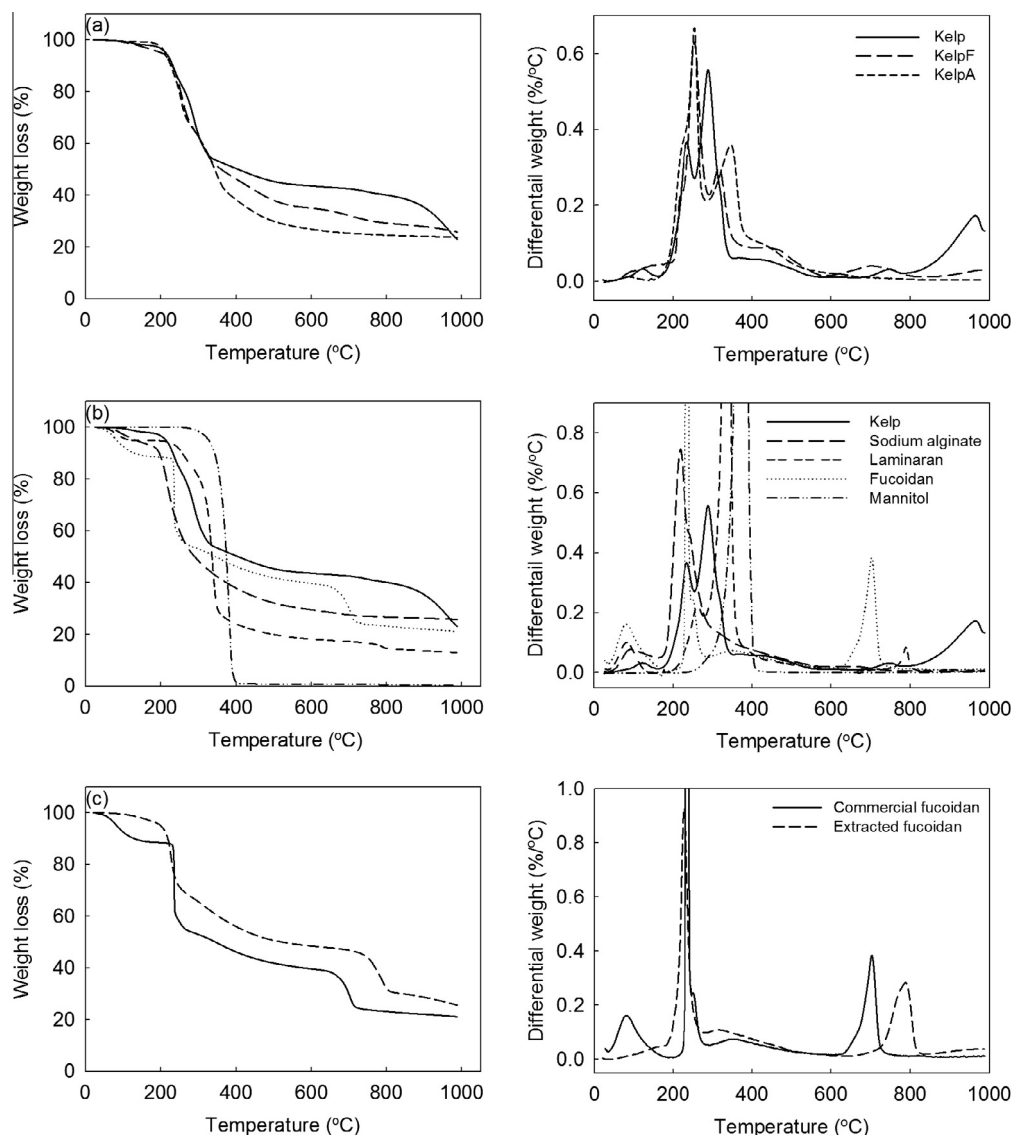
Fig. 3. Thermogravimetry (left) and differential thermogravimetry results (right) of (a) kelp powders, (b) the major components of kelp, and (c) fucoidan.

Table 2
Properties of pyrolysis oils.

	Kelp (S. japonica) oil	KelpF oil	KelpA oil
Yield (%)			
First condenser	9.1	5.6	6.4
Second condenser	28.8	23.0	26.9
Total	37.9	28.6	33.3
Density (g/cm³)			
First condenser	1.13	1.03	1.03
Second condenser	1.07	1.02	1.04
Water content (wt%)			
First condenser	34.7	73.0	64.8
Second condenser	82.4	82.4	79.3
Solid content (wt%)			
First condenser	0.133	0.290	0.185
Second condenser	0.035	0.033	0.030
TAN (mg KOH/g)			
First condenser (top layer)	43	73	129
First condenser (bottom layer)	56	62	101
Second condenser (top layer)	38	51	73
Second condenser (bottom layer)	45	33	90

The elemental compositions of the pyrolysis oils did not significantly depend on the pretreatment method, indicating that the pretreatment method did not affect the quality of the pyrolysis oils (Table 3). The difference in the compositions was distinct between the dark and the transparent oils. The carbon composition was large for the dark oils, at 60.2–72.2 wt%, O/C = 0.16–0.35 (mol/mol), and H/C = 1.4–1.7 (mol/mol). In comparison, the transparent oils exhibited a carbon composition of 5.5–25.2 wt%, O/C = 1.5–7.0 (mol/mol), and H/C = 4.5–20 (mol/mol). These observations indicate that the dark oils were hydrocarbon-rich and that the transparent oils were water-rich. The hydrocarbon-rich dark oils exhibited HHVs of 30.0–36.1 MJ/kg, which are much larger than those of the feedstocks and lignocellulosic pyrolysis oils and similar to those of fossil fuels [43].

The viscosities of the pyrolysis oils, measured using a cone-and-plate viscometer, exhibited shear-thinning non-Newtonian behavior at low shear rates, as reported for lignocellulose pyrolysis oils (Fig. 4) [23,44]. All of the pyrolysis oils in this study became Newtonian at a shear rate larger than $1–100\,\mathrm{s^{-1}}$. Compared to the non-treated kelp oil ($10^{-2}–1\,\mathrm{Pa\,s}$), both the KelpF and KelpA oils exhibited lower viscosities ($6 \times 10^{-3}–2 \times 10^{-1}\,\mathrm{Pa\,s}$ for the KelpF oil and $3 \times 10^{-3}–10^{-1}\,\mathrm{Pa\,s}$ for the KelpA oil). According to the

Table 3
Elemental compositions of pyrolysis oils.

Oil	Elemental composition (wt%)						O/C (mol/mol)	H/C (mol/mol)	HHV (MJ/kg)
	C	H	N	S	O	total			
Kelp									
First condenser (top layer)	69.2	8.3	3.7	<0.3	15.4	96.6	0.17	1.4	35.0
First condenser (bottom layer)	25.2	9.4	2.6	<0.3	49.9	87.1	1.5	4.5	14.3
Second condenser (top layer)	12.0	10.5	1.1	<0.3	56.1	79.7	3.5	10	10.4
Second condenser (bottom layer)	72.2	8.3	3.9	<0.3	15.3	99.7	0.16	1.4	36.1
KelpF									
First condenser (top layer)	10.5	10.6	2.7	<0.3	53.6	77.4	3.8	12	10.6
First condenser (bottom layer)	60.2	8.8	5.3	<0.3	28.2	102.5	0.35	1.7	30.0
Second condenser (top layer)	5.5	10.9	1.6	<0.3	51.1	69.1	7.0	24	10.1
Second condenser (bottom layer)	66.3	8.7	4.8	<0.3	18.0	97.8	0.20	1.6	34.2
KelpA									
First condenser (top layer)	19.0	9.8	2.5	<0.3	53.1	84.4	2.1	6.2	12.2
First condenser (bottom layer)	68.2	8.6	3.0	<0.3	20.3	100.1	0.22	1.5	34.1
Second condenser (top layer)	6.5	10.7	1.1	<0.3	53.8	72.1	6.2	20	9.40
Second condenser (bottom layer)	62.1	8.6	3.8	<0.3	24.0	98.5	0.29	1.7	31.2
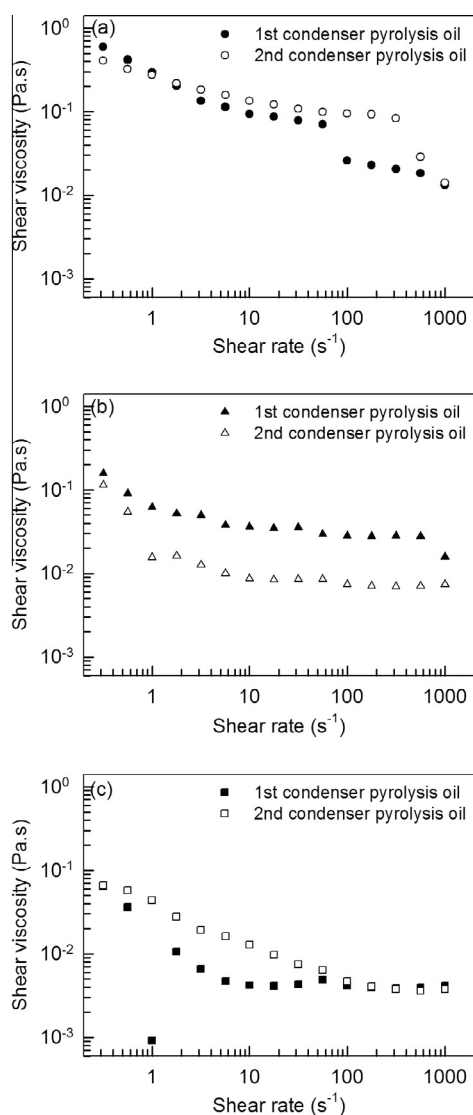
Fig. 4. Viscosities of the pyrolysis oils obtained from (a) Kelp, (b) KelpF, and (c) KelpA.

Fig. 5. GC/MS results of (a) the top and (b) bottom layers of pyrolysis oils dissolved in tetrahydrofuran. (Only reliable compounds are depicted.)

viscosities (Fig. 4) and the corresponding water contents (Table 3), the water content or the organic compounds' concentration did not seem to determine the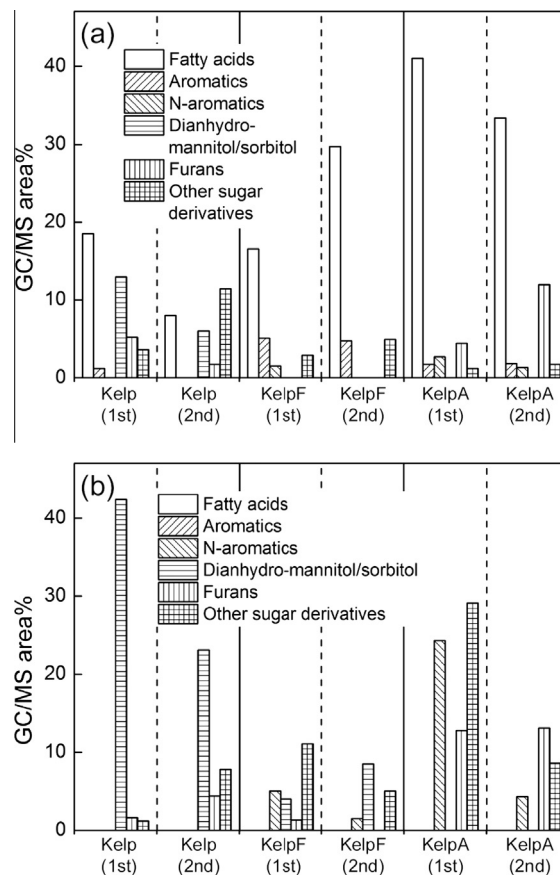 viscosities, but the chemical treatment methods adjusted the chemical structures of the pyrolysis oils. It was also observed that the KelpA oil exhibited lower viscosity compared to the KelpF oil, which may be attributed to the production of small kelp fragments during the acid treatment compared to the CaCl$_2$ treatment. Because the water contents are similar for the pyrolysis oils, except for the kelp oil collected in the first condenser, a low level of viscosity, lower than that of lignocellulosic pyrolysis oils, may improve the oil's transportation [43].

The produced Kelp, KelpF, and KelpA pyrolysis oils were dissolved in tetrahydrofuran (50% w/w) and further analyzed with

GC/MS to identify the oil components (Table S2, Figs. 5 and S5). After the addition of tetrahydrofuran to the oils, dark and transparent oil phases were found on the top and bottom layers, respectively, regardless of the kelp feedstock used. The dark oils on the top layers contained more hydrophobic compounds, including fatty acids and aromatic compounds, and the transparent oils on the bottom layers contained more hydrophilic compounds, including dianhydromannitol, dianhydrosorbitol, and sugar derivatives. The $CaCl_2$ and sulfuric acid treatments increased the amounts of fatty acids and decreased the sugar derivatives in the dark oils (top layers). In the transparent oils (bottom layers), the $CaCl_2$ and sulfuric acid treatments decreased the amounts of anhydrous dimers of mannitol and sorbitol. The sulfuric acid treatment increased the amounts of N-heteroaromatic compounds (pyridinol and pyrrolidinone) and furan derivatives.

When the pyrolysis oils were produced in the fixed-bed-type batch reactor, remaining biochar was observed (Fig. S6), indicating that the char from the non-treated kelp powder became bulky, whereas those from KelpF and KelpA contained smaller particles. These observations must be attributed to the pretreatment of the kelp, which softened the structures and removed the catalytic minerals. The elemental composition of the biochar was measured (Table S3), finding lower concentrations of minerals in KelpF and KelpA biochar compared to the non-treated kelp biochar. Thus, the calculated HHV of KelpA biochar was 27.6 MJ/kg, which was much higher than those of the non-treated Kelp and KelpF. The high HHV of the KelpA biochar suggests the possibility of using kelp biochar as a biocoal capable of producing less ash.

3.4. Continuous fluidized bed reaction

Based on observations of the oils produced through the batch reaction, the continuous fluidized bed reactor was operated using Kelp and KelpA. When the non-treated kelp was supplied to the reactor, a large amount of cylindrical char quickly formed in the middle of the fluidization bed (Fig. S1), which seriously suppressed its continuous operation, as discussed in the introduction section. KelpA, however, did not produce large chunks of char, only producing small char particles, which were collected at the cyclone. These observations indicate that the acid-treated kelp powder has better processability in the continuous fluidization bed reactor.

As discussed in the introduction section and observed in Figs. S1 and S6, the pyrolysis of macroalgae is difficult, possibly on account of polymerization or carbonization during the pyrolysis by existing inorganic minerals or polysaccharides, as reported in the literature [6]. In this study, inorganic elements were removed using a sulfuric acid pre-treatment to produce pyrolysis oil efficiently because inorganic elements, not sources for oils, may catalyze the polymerization of organic compounds during the pyrolysis process [6].

4. Conclusions

Considering rapidly growing biochar in continuous fluidization bed reactors, a pretreatment of macroalgae feedstocks was performed in an effort to reduce the formation of process-hindering large chunks of biochar in the middle of the fluidization bed. From observation of the pyrolysis oils and the continuous reactor, the sulfuric acid pretreatment methods (i) improved the operation of continuous pyrolysis process of kelp and (ii) suppressed the formation of biochar. The suppressed formation of biochar was clearly observed when the sulfuric-acid-treated kelp powder was used as a feedstock because the inorganic elements, which may catalyze the growth of biochar, in the kelp powder were removed by the acid treatment. Sulfuric acid pretreatment also increased the fatty acid composition in the pyrolysis oil, with less formation of bulky char. The better processability of the kelp pretreated with sulfuric acid was attributed to the removal of catalytic minerals and the softening of the kelp structure.

Acknowledgement

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.enconman.2014. 04.094.

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